New England States. If all the water power of the United States were to be similarly developed, it would probably be necessary to install plants having three or four times the capacity of the estimated minimum potential water power as given in the table. This condition should be fully considered in estimating the amount of potential water power that may still be available in any State at the present time.

SPECIAL ARTICLES

THERMIONIC EFFECTS CAUSED BY ALKALI VAPORS IN VACUUM TUBES

A TUNGSTEN filament was mounted in a vacuum tube in the axis of a cylindrical anode consisting of three parts insulated from one another. In this way, on the guard ring principle, the electron emission from the central portion of the filament could be measured, so that effects due to the cooling by the leads were eliminated. With metallic cæsium in the tube at 25° C. the cæsium vapor forms an adsorbed film consisting of a single layer of atoms completely covering the filament even at filament temperatures of 600° K. or more. The stability of this film appears to be due to the fact that the electron affinity of a tungsten surface (Richardson work function, 4.52 volts) is greater than that of cæsium ions (ionizing potential, 3.90 volts). When a cæsium atom comes close to a tungsten surface, the tungsten thus robs the cæsium atom of its valence electron and leaves it in the form of a univalent positive ion. This ion, however, tends to be held by a strong force to the tungsten surface because of the negative charge induced in the metallic surface by the close proximity of the positive charge of the ion.

The presence of such films is shown experimentally by the very high electron emission and by measurement of the contact potential with respect to a second tungsten filament held at such temperature that the cæsium has evaporated off.

In the presence of minute traces of certain electro-negative gases, adsorbed films of the atoms of these gases are formed on the tungsten, resulting in an increase in the electron affinity of the surface and a corresponding decrease in the normal electron emission (in absence of cæsium). But the tendency of the cæsium to be held by such a surface has thereby been increased, with the result that the cæsium film remains on the surface at an even higher filament temperature. The film then consists of two layers, each of atomic thickness, the first being of electro-negative, the second of electro-positive atoms (ions).

In this way the cæsium film remains intact up to temperatures of about 900° K., and at this temperature (below a visible red heat) emits saturation currents of about 0.3 amperes per square cm. of filament surface. At higher temperatures the cæsium film evaporates off in part and the electron emission falls rapidly. On lowering the temperature the cæsium film reforms and the electron emission returns to its former value. At temperatures below those at which evaporation is appreciable, the saturation current from a cæsium-covered surface is expressed within the probable error of temperature measurement, by Dushman's equation,

$$i = 60.2\ T^2 e^{-b_0/T}\ \textit{amps. per cm.}^2$$

where $b_0 = 16000$ degrees. This corresponds to a value of 1.38 volts for the Richardson work function. It is of interest to note that b_0 appears to be practically the same whether the cæsium is adsorbed directly on tungsten or on the adsorbed electro-negative film. The electron emission thus depends primarily on the nature of the atoms forming the actual surface layer and is not materially dependent on the atoms that lie under these.

When a tungsten filament is heated above 1000° K. in cæsium vapor at room temperature, the electron emission falls to negligible values although a large fraction of the surface may still be covered with adsorbed cæsium. This is due to the fact that there is a linear relation between Θ, the fraction of the surface covered by cæsium, and the logarithm of the saturation current. At 800° K. the ratio between the emission from a cæsium film ($\Theta = 1$) and from a pure tungsten surface is about 10^{20}. Thus every change of 0.05 in the value of Θ causes a ten-fold change in the emission. By the time Θ has fallen to 0.7 the emission at 800° or 900° is negligible.

When the cæsium evaporates from the surface film at temperatures in the neighborhood of 1,000° K. it does so in the form of neutral atoms. Although the electron affinity of a pure tungsten surface is greater than that of the cæsium atom the electron affinity of a surface *partly covered by cæsium* may be less. This does not prevent the cæsium in the surface film being in the form of ions, for the electron affinity that is involved in the formation and stability of these ions in the surface is not that of the surface of the filament but rather that of the pure tungsten layer underlying the cæsium film. As the cæsium ions evaporate from a largely covered surface they take up electrons as soon as they get out of the surface film, for the filament surface, from the position they are then in, has less electron affinity than the ions.

The electron affinity of a surface partly covered with cæsium is a linear function of Θ as follows:

$$\varphi_{\Theta} = \varphi_w - \Theta(\varphi_w - \varphi_{cs})$$

where φ_w, φ_{cs}, are respectively the electron affinities of pure tungsten and a cæsium film, while φ_{Θ} is the electron affinity of the surface when Θ is the fraction of its surface covered by cæsium. Placing $\varphi_w = 4.52$ volts; $\varphi_{cs} = 1.38$ volts and making φ_{Θ} equal to the ionizing potential of cæsium (3.90 volts) we find $\Theta = 0.20$. Therefore when 20 per cent. of a tungsten surface is covered by cæsium atoms, the electron affinity of the surface is the same as that of cæsium ions.

Thus when the filament temperature is raised to a point such that Θ is in the neighborhood of 0.2, positive ions begin to escape from the filament without combining with electrons. This result, first found experimentally, occurs at a certain critical temperature in the neighborhood of 1150° K., depending to some extent on the pressure of cæsium vapor and the condition of the filament surface.

The surface of the filament is in one of two states which we may denote by α and β and the transition between these is discontinuous. At a given time part of the filament may be in one state while an adjacent part at the same temperature is in the other state, there being a sharp *boundary* between the two regions which boundary may be made to move along the filament at any desired velocity.

In the α state Θ is more than 0.2, the surface being largely covered by cæsium. The cæsium evaporates in the form of neutral atoms, although as the critical temperature is approached an increasing fraction may leave as positive ions.

In the β state Θ is ordinarily very much less than 0.2 and all cæsium which leaves the surface is in the form of *positive* ions. Since every atom that strikes the surface condenses, the rate of production of positive ions is equal to the rate at which cæsium atoms strike the filament. Thus from the kinetic theory we calculate that the saturation positive current i_+ is

$$i_+ = \frac{ep}{\sqrt{2\pi mkT}} = 0.367\frac{p}{\sqrt{T}} \text{ amps./cm.}^2$$

where p is the pressure of cæsium vapor in bars, m is the mass of an atom of cæsium, e the charge of an electron, k the Boltzmann constant and T is the absolute temperature of the bulb. The rate of generation of positive ions is thus independent of the filament temperature provided this is above the critical temperature. It is also the same for all filament materials which give the effect. It is proposed that any electrode which *gen*erates positive ions be called a *genode.*

Experiments show that the maximum positive ion currents obtainable from a genode are in fact, above a certain temperature, independent of the genode temperature, are proportional to the vapor pressure in accordance with the above equation, and are the same for tungsten, molybdenum, carbon or nickel.

It is necessary to apply a certain negative voltage to the cylinder to draw off all the ions generated by the genode. Above this voltage the currents appear to be absolutely independent of voltage (much more so than in the case of electron emission). Below this voltage the positive ion current is limited by space charge, the current being proportional to the 3/2 power of the voltage but being smaller than in the case of electron currents between similar electrodes in the ratio of the square roots of the masses of the electron and the cæsium ion (1 : 490).

The measurement of the ion generation affords an apparently extremely accurate method of determining the vapor pressures of alkali metals. For example at a bulb temperature of 24° C. the maximum positive ion current in cæsium vapor is 32×10^{-6} amps./cm.^{2} from which the vapor pressure is calculated, by the equation given above, to be 0.00166 bar.

The conditions near the critical temperature, where both the α and β surface phases may be present together, are probably analogous to those assumed in van der Waals' theory of the transition between liquid and gas. In the β phase near the critical temperature there is probably an atmosphere, extending out to a distance of several Ångstrom units from the surface of the filament, containing electrons and a slight excess of positive ions. If the temperature is lowered the attractive forces cause a condensation to the α phase which has a much higher concentration of positive ions. At still lower temperatures, the ions probably settle down into a definite monatomic adsorbed film. Under proper conditions the velocity of propagation of the boundary between the two phases has been observed experimentally.

If a thoriated tungsten filament is used in experiments with cæsium vapor it is found that both the electron emission and the ion generation disappear if the filament is first given a heat treatment by which an adsorbed film of thorium is brought to the surface. This result is in full accord with the theory outlined above, for the electron affinity of a fully active thoriated filament is only 2.94 volts. Since this is less than the electron affinity of the cæsium ion we should not expect the cæsium atoms to lose their electrons when they strike the surface. A quantitative study is being made of the phenomena occurring when various proportions of the surface are covered by thorium.

Similar effects to those described in this paper have also been observed with other alkali metal vapors, notably rubidium vapor. The ionizing potentials of these vapors are higher and the vapor pressures lower, so that the effects tend to be less marked. The results, however, confirm the theories which so well explain the behavior of cæsium.

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THE OXIDATION OF SELENIUM BY A NEW GROUP OF AUTOTROPHIC MICROORGANISMS

THE discovery of the nitrifying and sulfur-oxidizing bacteria by Winogradsky added much to our knowledge on energy transformation in the metabolism of the living cell. Here were organisms that were able to obtain from the oxidation of purely inorganic substances all the energy necessary for their activities and for the assimilation of the carbon from the carbon dioxide of the atmosphere or from carbonates. The hydrogen, methane and iron bacteria were soon added to these groups of autotrophic microorganisms. However, some of these organisms seem to be able to exist also in the presence of organic matter, from which they can derive their energy, as pointed out by Niklewsky for the methane bacteria, Molish for the iron bacteria and purple sulfur bacteria, Beijerinck and Trautwein for the denitrifying colorless, sulfur oxidizing organisms.

Among the strictly (obligate) autotrophic bacteria, which derive their energy only from the oxidation of the inorganic materials, are the nitrite and nitrate bacteria, as pointed out by Meyerhof, and the sulfur oxidizing organism *Thiobacillus thiooxidans* described recently by the writers, which derives its energy from the oxidation of elementary sulfur, thiosulfates and sulfides.

Another group of organisms can now be added to the list of the autotrophic forms, namely, bacteria which are able to derive their energy from the oxidation of selenium. A small quantity of selenium mixed with fresh soil was slowly oxidized with an increase in soil acidity. When some of this soil was added to a culture medium, consisting of inorganic materials, with elementary selenium as the only source of energy, the medium became cloudy within a few days. There appeared in it a minute, rod shaped bacterium capable of oxidizing selenium to selenic acid. A detailed description of the organism as well as of the methods used in its isolation will be published later.

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